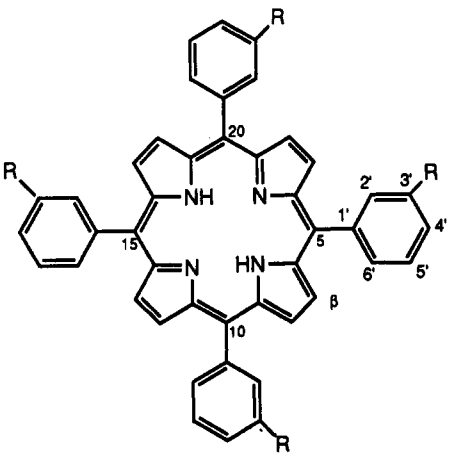
outside the cavity (Figure 1).[16] This suggests that, in the absence of strong interactions between the solvent and the solute, these porphyrins in solution will exist in a symmetrical conformation and their ^1H NMR will be assignable as shown for 4 in the data of ref 13. Since 5 is not soluble in $CDCl_3$, its ^1H NMR spectrum was taken in DMSO-d_6 and acetone-d_6. The ^1H NMR in DMSO-d_6 shows four NH signals in the region from δ -5.2 to -6.1, two benzylic proton signals, and two methylic proton signals in the region δ 4.8–5.7 and a complex aromatic region from δ 7.0 to 10.0.[17] In contrast, the ^1H NMR spectra of the corresponding tetraprotonated species (prepared by adding excess trifluoroacetic acid to 5) in different solvents (acetone-d_6, DMSO-d_6, CD_3OD, and CF_3COOD) show assignable peaks. For example, the ^1H NMR in acetone-d_6 shows a pyrrolic NH proton at δ -4.3, a broad signal at δ 5.0 corresponding to the benzylic and methylic protons and integrating 28 protons, four phenylic proton signals at δ 7.1, 7.9, 8.0, and 8.2 each integrating 8 protons, one meso signal at δ 8.25 integrating 16 protons, and four pyridinic proton signals at δ 8.75, 9.4, 9.7, and 10.1 each integrating 4 protons. These results are anticipated from the structure of tetraprotonated 5.

Comparison of the ^1H NMR spectrum of 5 to that of its biszinc and tetraprotonated derivatives in DMSO shows a dramatic conformational switch between them. This indicates that DMSO interacts with the porphyrin moieties and this interaction is inhibited by inducing species such as Zn^{2+} or H^+ in the center of the porphyrin rings. The same phenomenon was observed with other dimeric porphyrins such as 4 and 6. The conformational change on transfer from $CDCl_3$ to DMSO-d_6 with these dimeric porphyrins can also be observed from their UV/vis spectra by the blue-shifting of the Soret band and red-shifting of visible bands (see table). The emission spectrum of the dimeric porphyrin 4 in DMSO is red-shifted and its intensity is increased by 30% compared to that in $CHCl_3$, whereas the emission spectrum of the monomeric porphyrin 7 in DMSO is unchanged and its intensity is 90% higher than that in $CHCl_3$. The increase in the intensity of the emission band by DMSO is due to general solvent



2 R = CH_2Br

7 R = CN

effects which are dependent on the dielectric constant of the solvent.[18] The relatively low effect of DMSO on the intensity of the emission bands in the dimer may be attributed to a specific interaction between DMSO and the fluorophore molecules of the dimer. Monomeric porphyrins such as 2 and 7 do not show any ^1H NMR or UV/vis spectral changes upon switching from $CDCl_3$ to DMSO-d_6. Varying the concentration of all the dimeric porphyrins examined from 1×10^{-2} to 5×10^{-6} M caused no change in the UV/vis and ^1H NMR spectra. The combined results reveal that the source of the effect seen in DMSO solutions is a result of an interaction between DMSO and the two porphyrin rings in the dimer, rather than aggregation,[19] and this interaction causes the two porphyrin rings to approach closer to each other as judged by the upfield shift of the pyrrolic N–H resonance and the quenching of the emission band intensity. Further work is currently underway to explore this phenomenon and to prepare other metal complexes of 5 for studies in aqueous and organic solutions.

Acknowledgment. This work was supported from grants from PROTOS corporation and the National Institutes of Health.

(16) The starting geometries of structures 4, 5, and Zn_2–5 were generated in the 2D molecular construction routine of Quanta (Polygen, Corp.) using the X-ray file of tetraphenylporphyrin (TPP) and minimized structures of pyridinesulfonamide and its *N*-methyl derivative and they were extensively minimized in $CHARM_m$ with steepest descents and adopted basis Newton-Raphson.

(17) Similar spectrum was obtained using acetone-d_6 as a solvent.

(18) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983; Chapter 7.

(19) The same phenomenon was observed in acetone.

Synthesis and Conformational Behavior of Fenestrindans (Tetrabenzo[5.5.5.5]fenestranes) with Four Bridgehead Substituents[1]

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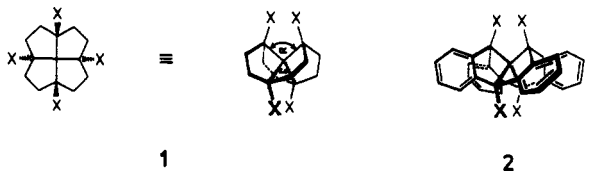
Summary: *all-cis*-Tetrabenzo[5.5.5.5]fenestranes (fenestrindans) with four bridgehead substituents (4-10) and two doubly bridged, centrohexacyclic analogues, the bis-*endo*-peroxide 11 and the bis-disulfide 12, have been synthesized from the tetrabromofenestrindan 3. Pronounced steric interactions between the substituents at opposite bridgehead positions have been revealed by NMR and DNMR spectrometry, showing remarkable size-dependent hindrance of the degenerate interconversion of the two S_4 symmetric conformers of the fenestrindans.

Fenestranes have attracted much interest because of the geometric constraints induced by the mutual fusion of the

(1) (a) Benzoannelated Centropolyquinanes, Part IX. Presented in part at the Sixth European Symposium on Organic Chemistry (ESOC VI), Belgrade, Yugoslavia, 1989, paper B-O 017. Part VIII: Paisdor, B.; Kuck, D. *J. Org. Chem.*, in press. (b) For a review on centropolyindans, see: Kuck, D. In *Quasicrystals, Networks, and Molecules of Fivefold Symmetry*; Hargittai, I., Ed.; VCH Publishers: New York, 1990; Chapter 19.

0022-3263/91/1956-3472$02.50/0

Scheme I



1 2

Scheme II

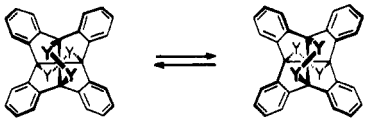
3

	4	5	6	7	8	9	10
X =	Cl	CH_3	F	OH	N_3	CN	SCH_3

four rings at a common, tetracoordinated carbon atom. In particular, the flattening of the rigid molecular framework at the central carbon atom has been studied.[2-4] The degree of angular or "planoid" distortion[4] has been evaluated in recent papers, which concentrate on the effects of ring size, unsaturation, and ring fusion stereochemistry at the molecular periphery, that is, at the bridgehead positions. For the latter factors, [5.5.5.5]fenestranes appear most attractive because several synthetic routes to them have been developed in recent years.[1b,2,5-7,10g]

Bridgehead substitution constitutes another structural feature that should affect the geometry of the fenestrane skeleton. The four substituents X in the as yet unknown *all-cis*-[5.5.5.5]fenestranes (1) form two pairs of syn-oriented atoms or atomic groups (Scheme I), the interaction of which could lead to skeletal torsion and/or changes in the two unbridged bond angles (α) at the central carbon atom.[4b,5e] Fenestranes bearing bridgehead substituents are very rare, and only three derivatives with two substituents at opposite bridgehead positions have been described.[8,9] However, to the best of our knowledge, no fenestranes with *four* independent, i.e. nonbridging,[9] substituents have been reported to date, with the exception of the recently synthesized tetrabromo derivative 3 of tetrabenzo[5.5.5.5]-fenestrane 2 (X = H, fenestrindan).[7a,10a] We report here on the synthesis of several new fenestrindans with four identical bridgehead substituents, 4–10, and two heterobridged analogues, 11 and 12, as well as on some preliminary results concerning their stereochemical properties.

Scheme III



11 12

Y = O S

Tetrabromofenestrindan 3, as a 4-fold benzhydryl halide, readily undergoes S_N1-type reactions under hydrolytic or Lewis acid assisted conditions. The tetrachlorofenestrindan 4 is obtained in 90% yield by reaction with excess $HCl/AlCl_3$ and forms, as do all the new fenestrindans reported here, a stable, crystalline material.[11,12] The tetrabromide 3 does not react readily with methylmagnesium bromide or methyllithium, but the 4-fold methyl-substituted fenestrindan 5 is obtained in good (73%) yield upon treatment with trimethylaluminium at rt for 10 min. The synthesis of tetrafluorofenestrindan 6 from a suspension of 3 and AgF in acetonitrile requires ultrasound to afford a moderate (ca. 40%) yield. The reaction is extremely sensitive to moisture, but the crystalline product 6, obtained after separation by MPLC, is stable both thermally and toward hydrolysis in normal atmosphere. Hydrolysis of the tetrabromide 3 in aqueous

(2) (a) Rao, V. B.; Agosta, W. C. *Chem. Rev.* **1987**, *87*, 399–410. (b) Krohn, K. *Nachr. Chem. Techn. Lab.* **1987**, *35*, 264–266. (c) Keese, R. *Ibid.* **1982**, *30*, 844–849.

(3) Krohn, K. In *Organic Chemistry Highlights*; Mulzer, J., Altenbach, H.-J., Braun, M., Krohn, K., Reissig, H.-U., Eds.; VCH Verlagsgesellschaft: Weinheim, 1991; pp 371–377.

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(7) (a) Kuck, D.; Bögge, H. *J. Am. Chem. Soc.* **1986**, *108*, 8107–8109. (b) Kuck, D., to be published. (c) Seifert, M. Doctoral Thesis, University of Bielefeld, 1991.

(8) Crimmins, M. T.; Mascarella, S. W.; Bredon, L. D. *Tetrahedron Lett.* **1985**, *26*, 997–1000.

(9) Mani, J.; Schüttel, S.; Zhamg, C.; Bigler, P.; Müller, C.; Keese, R. *Helv. Chim. Acta* **1989**, *72*, 487–495.

(10) Fenestranes with one or two homo- or heterocyclic bridges between bridgeheads have been reported. See refs 6a and 6b as well as the following: (a) Kuck, D.; Schuster, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1192–1194. (b) Kuck, D.; Paisdor, B. 200th ACS National Meeting, Washington, D.C., 1990, Paper ORGN 316. (c) Paisdor, B. Doctoral Thesis, University Bielefeld, 1989. (d) Schuster, A. Doctoral Thesis, University Bielefeld, 1991. (e) Simmons, H. E., III; Maggio, J. E. *Tetrahedron Lett.* **1981**, *22*, 287–290. (f) Paquette, L. A.; Vazeux, M. *Ibid.* **1981**, *22*, 291–294. (g) Paquette, L. A.; Williams, R. V.; Vazeux, M.; Browne, A. R. *J. Org. Chem.* **1984**, *49*, 2194–2197. (h) Pfenninger, A.; Roesle, A.; Keese, R. *Helv. Chim. Acta* **1985**, *68*, 493–507. (i) Fessner, W.-D.; Sedelmeier, G.; Spurr, P. R.; Rihs, G.; Prinzbach, H. *J. Am. Chem. Soc.* **1987**, *109*, 4626–4642. (j) Melder, J.-P.; Fritz, H.; Prinzbach, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 300–303. (k) Pinkos, R.; Rihs, G.; Prinzbach, H. *Ibid.* **1989**, *28*, 303–305.

(11) All new fenestrindans reported here, except 7, gave satisfactory combustion analyses (±0.4%). The identity of 7, which was found to cocrystallize with THF, has been confirmed by high-resolution mass spectrometry.

(12) Selected physical data of the new compounds, 4: colorless needles; mp 325–330 °C dec; ^1H NMR (see Figure 1b; $CDCl_3$) δ 7.88 (d, ^3J = 6.5 Hz, 4 H), 7.55–7.45 (m, 12 H), ABCX spin system; ^{13}C NMR ($CDCl_3$) δ 144.7 (q), 140.9 (q), 130.3 (t), 130.1 (t), 125.5 (t), 123.0 (t), 88.1 (q, *centro*-C), 79.6 (q). 5: colorless crystals; mp 341 °C; ^1H NMR ($CDCl_3$) δ 7.48 (d, ^3J = 7.1 Hz, 4 H) and 7.33–7.21 (m, 12 H), ABCX spin system, 1.25 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 151.8 (q), 146.3 (q), 127.5 (t), 127.1 (t), 123.7 (t), 121.6 (t), 88.3 (q, *centro*-C), 58.9 (q), 28.3. 6: white powder of extremely low solubility and mp >395 °C dec; ^1H NMR (DMSO-d_6) δ 7.91 (8 H) and 7.64 (8 H), AA'BB' spin system; ^{13}C NMR (DMSO-d_6, 50 °C) δ 140.7 (q), 131.0 (t), 123.6 (t), "aliphatic" signals are missing due to low concentration; ^{19}F NMR (DMSO-d_6) δ −139.5 (s). 7: colorless crystals containing some THF; mp 305 °C dec; ^1H NMR (see Figure 1a; $CDCl_3$) δ 7.68 (8 H) and 7.44 (8 H), AA'BB' spin system, 4.10 (4 H); ^{13}C NMR ($CDCl_3$) δ 145.4 (q), 129.7 (t), 124.0 (t), 90.3 (q), 78.4 (q, *centro*-C). 8: crystalline powder (**which explodes upon shock or heating!**); decomposes at ca. 215 °C; ^1H NMR (pyridine-d_5, 40 °C) δ 7.65 (4 H), 7.54 (12 H), two broadened signals (cf. Figure 1c); ^{13}C NMR (pyridine-d_5) δ 142.3 (q), 131.0 (t), 125.3 (t), 80.6 (q). The signal for the central C atom is extremely low and has not been identified unambiguously. 9: white powder; mp 288 °C dec; ^1H NMR ($CDCl_3$) δ 7.97 (d, ^3J = 8.1 Hz, 4 H), 7.65 (m, 12 H), ABCX spin system; ^{13}C NMR ($CDCl_3$) δ 137.8 (q), 137.3 (q), 132.02 (t), 132.00 (t), 125.9 (t), 125.1 (t), 117.1 (q), 56.6 (q); the signal for the central C atom is missing. 10: white solid; mp 292 °C; ^1H NMR ($CDCl_3$) δ 7.90 (d, ^3J = 7.6 Hz, 4 H), 7.34 (m, 12 H), ABCX spin system, 0.81 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 145.8 (q), 142.5 (q), 128.6 (t), 127.8 (t), 126.7 (t), 124.3 (t), 69.6 (q), 14.7 (p), the signal for the central C atom is missing. 11: colorless crystals; mp 230 °C dec; ^1H NMR ($CDCl_3$) δ 7.63 (8 H), 7.44 (8 H), AA'BB' spin system; ^{13}C NMR ($CDCl_3$) δ 142.6 (q), 131.0 (t), 125.6 (t), 123.9 (q, *centro*-C), 100.6 (q). 12: colorless crystals; mp >370 °C; ^1H NMR (see Figure 1c, $CDCl_3$) δ 7.7 (br, <8 H) and 7.47 (br s, >8 H); ^{13}C NMR δ 142.2 (q), 129.9 (t), 123.7 (t), 99.4 (q, *centro*-C), 84.3 (q).

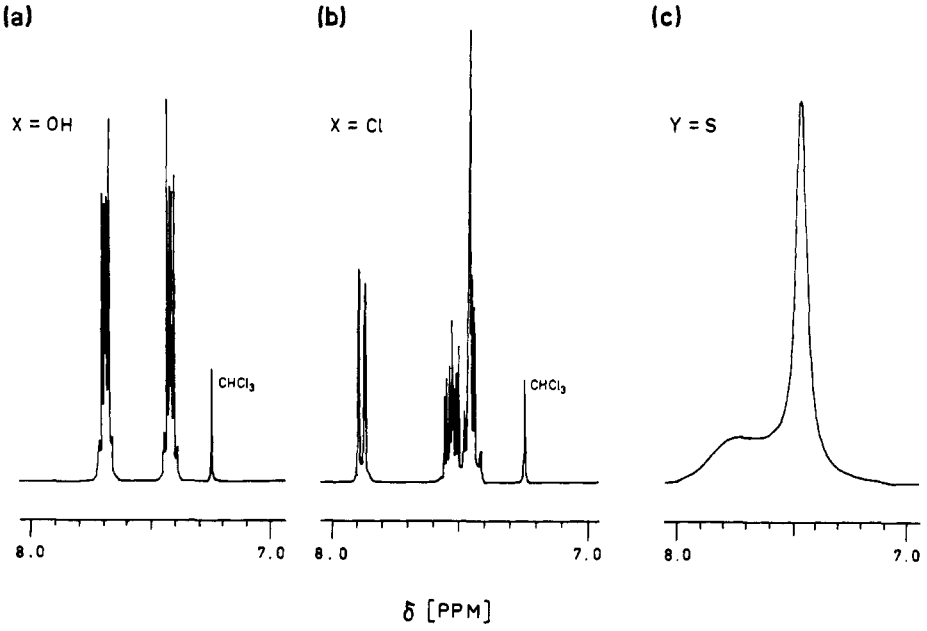

Figure 1. ^{1}H NMR spectra (300 MHz, $CDCl_3$, 30 °C) of (a) tetrahydroxyfenestrindan (7), (b) tetrachlorofenestrindan (4), and (c) of bis-disulfide 12.

sulfuric acid/THF gives the tetraalcohol 7 in good yield.[13] Alkaline hydrolysis, by contrast, does not afford satisfactory yields.

In analogy to other activated alkyl halides,[14] tetrabromofenestrindan 3 reacts with trimethylsilyl (TMS) azide and with other trimethylsilyl "pseudohalides" like TMS cyanide and methyl TMS sulfide under catalysis with $SnCl_4$ in methylene chloride. Remarkably, the tetraazidofenestrindan 8 has been obtained in good yields as a crystalline solid, which is, as expected, highly sensitive to thermal treatment and mechanical shock. Analogous reactions of 3 with TMS cyanide and methyl TMS sulfide give the fourfold bridgehead nitrile 9 and tetrathioether 10. The latter two conversions have not been optimized yet but promise the possibility of inducing various bonding interactions between opposite bridgehead functionalities.

By Ag(I) *ion assisted reaction of tert-butylhydroperoxide*,[15] 3 can be converted to the bis-*endo*-peroxide 11, which represents a new centrohexacyclic (topologically non-planar) molecule, reminiscent of the Simmons–Paquette molecule[10e-g] and of centrohexaindan.[10a-d] Peroxide 11 readily crystallizes from THF solutions in beautiful, half-inch, thin plates. The analogous bis-disulfide 12 has been obtained by reaction of 3 with elemental sulfur at 250 °C in 40% yield. The synthesis of further tetrathiahexacycles as well as other heterobridged fenestrindans is under current investigation in our laboratory.

The ground-state conformation of solid fenestrindan 2 (X = H) has S_4 molecular symmetry, but the two S_4 forms interconvert rapidly in solution, giving rise to degenerate NMR resonances corresponding to the formal D_{2h} symmetry.[7a,16] The ^{1}H and ^{13}C NMR spectra of the substituted fenestrindans 3–12 clearly reflect the two types of molecular symmetries, depending on the individual bridgehead substituents. Three typical examples are reproduced in Figure 1. For small substituents (X = F and OH), the NMR spectra show simple AA'BB' proton spin coupling (cf. 7, Figure 1a) and only three arene ^{13}C resonances, respectively. Not surprisingly, the bis-*endo*-peroxide 11 shows the same behavior; thus rapid interconversion occurs in all three cases in rt solutions. By contrast, fenestrindans 3,[10a] 4 (Figure 1b), and 8–10 all exhibit ABCX spin systems with characteristic downfield doublets representing four ortho protons, and six 4-fold-degenerate ^{13}C arene resonances. Hence, in these cases the interconversion of the S_4 conformers is slowed down or almost suppressed at least at ambient temperatures. The rt ^{1}H NMR spectrum of the bis-disulfide 12 (Figure 1c), as a borderline case, displays two broad, nearly coalescenced signals, whereas only three ^{13}C lines are observed for the benzo nuclei.

The dynamic behavior within the series 3–12 appears to be very different. The observation of "static" conformers on the NMR time scale for the fenestrindans 3–5 and 8–10 demonstrates that the interconversion of the S_4 rotamers is drastically hindered by unfavorable steric interactions within each pair of bridgehead substituents. In fact, no coalescence is observed upon heating both 3[10a] and 4 to 120–130 °C in $C_2D_2Cl_4$, indicating that the activation barrier toward interconversion of the two rotamers is >100 kJ·mol^{-1}.[21] The ^{1}H NMR spectrum of tetramethylfenestrindan 5 shows significant signal broadening at those temperatures, and coalescence is observed at 65 °C in its ^{13}C NMR spectrum (activation parameters: ΔG^*_{298} = 69 ± 10 kJ·mol^{-1}, ΔH^* = 49 ± 10 kJ·mol^{-1}, and ΔS^* = 70 J·mol^{-1}·K^{-1} [22]).

(13) Tetrol 7 has been prepared also by reaction of fenestrindan 2 (X = H) with dimethyldioxirane and methyl(trifluoromethyl)dioxirane: Curci, R.; Fusco, C.; Schuster, A.; Kuck, D., to be published.

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(16) Similar conformational distortions of the formal molecular symmetry have been found for other solid centropolyindans (ref 17) and for [5.5.5.5]fenestranetetrone (stauranetetrone, ref 18) and have been calculated for several centropolyquinanes (refs 19, 20).

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(22) The coalescence of the two adjacent resonances of the meta nuclei (δ 127.5 and 127.1 ppm) was evaluated.

The results presented here show that a range of fenestranes with fourfold bridgehead substitution has become synthetically accessible. The NMR data clearly reveal that the barrier to conformational interconversion, and thus the unfavorable steric and, probably, dipolar interactions, increase in the order F, OH ≪ CH_3 ≪ CN, N_3, SCH_3, Cl, Br, much different from substituent trends in substituted cyclohexanes.[23] We feel that **2** represents an interesting parent system to study both dynamic and static effects of bridgehead substituents on the fenestrane framework. Preliminary force-field calculations suggest that the "planoid" distortions at the central carbon atoms of fenestrindans **3–12** are considerably affected by the nature of the bridgehead substituents.[24] Detailed investigations are underway including X-ray crystal structure analysis of bridgehead-substituted fenestrindans.

Acknowledgment. We are grateful to Professor H.-F. Grützmacher for support of our research and to Mr. K.-P. Mester and to Dr. B. Paisdor for performing, and for help evaluating, the dynamic NMR measurements. We thank Professor J. M. Cook for a preprint (ref 5e). Financial support by the Deutsche Forschungsgemeinschaft (Ku 663/1-1) is greatfully acknowledged.

Supplementary Material Available: Full experimental and spectrometric data of compounds **4–12** (6 pages). Ordering information is given on any current masthead page.

(23) March, J. *Advanced Organic Chemistry, Reactions, Mechanisms, and Structure*, 3rd ed.; John Wiley & Sons: New York, 1985; pp 125–126.

(24) MMPMI and MM2(87) force-field calculation programs (QCPE, University of Indiana, Bloomington) both gave α = 112.5° for **2** (X = H, Scheme 1), considerably lower than the X-ray value α = 116.5° [7a], and a gradual increase of α up to 117–118° for X = Cl and Br.

Articles

Homolytic Alkylation of Enamines by Electrophilic Radicals[1]

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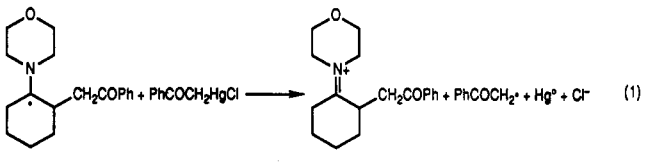
Received November 6, 1990

The electrophilic radicals R• = p-$O_2NC_6H_4CH_2$• or $Me_2C(NO_2)$• add readily to $CH_2{=}C(NMe_2)_2$ to yield $RCH_2C(NMe_2)_2$•, which undergoes electron transfer with p-$O_2NC_6H_4CH_2Cl$ or $Me_2C(NO_2)_2$ to regenerate R•. Hydrolysis yields p-$O_2NC_6H_4CH_2CONMe_2$ and $Me_2C{=}CHC(NMe_2)_2^+$, respectively. p-Nitrobenzyl radicals add readily to *N*-pyrrolidino- or *N*-morpholino-1-cycloalkenes to yield after hydrolysis the α-(p-nitrobenzyl)cycloalkanones. Photostimulated alkylation of *N*-pyrrolidino-1-cycloalkenes by $Me_2C(NO_2)_2$ is not observed although in competitive reactions between the enamine and $Me_2C{=}NO_2Li$, the product from attack of $Me_2C(NO_2)$• upon the enamine double bond is formed. The *N*-pyrrolidino-1-cycloalkenes are more reactive toward p-$O_2NC_6H_5CH_2$• than their morpholino analogues.

Introduction

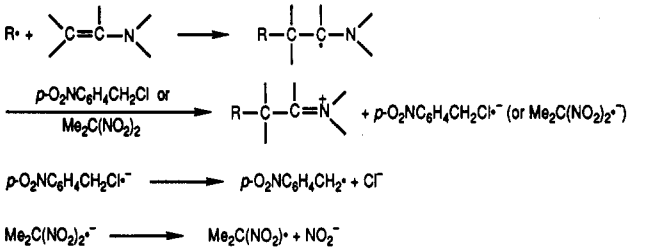
The free-radical chain reaction between $PhCOCH_2HgCl$ and 1-morpholinocyclohexene has been reported to involve addition of the acceptor radical $PhCOCH_2$• to the electron-rich double bond of the enamine followed by the electron transfer of reaction 1.[2] Perfluoroalkyl halides are also recognized to react with enamines by a radical chain process presumably involving electron transfer.[3,4]



(1)

Attempts to utilize simple alkylmercury halides in photostimulated reactions with enamines failed to yield the alkylation products observed with $PhCOCH_2HgCl$, presumably because facile addition to an electron-rich system requires an electrophilic radical. In a search for further examples of radical alkylations of enamines, we have examined reactions with p-$O_2NC_6H_4CH_2Cl$ and $Me_2C(NO_2)_2$, substrates known to react with a variety of anions in a free-radical chain sequence.[5,6] Photostimulated alkylation reactions were indeed observed between these substrates and various enamines. With p-$O_2NC_6H_4CH_2Cl$

Scheme I (R = $Me_2C(NO_2)$ or p-$O_2NC_6H_4CH_2$)



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